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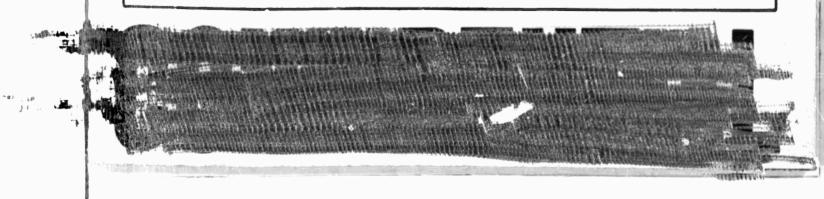# AD

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NAVORD REPORT 6206

COMPOUNDS CONTAINING THE TERMINAL FLUORODINITROMETHYL GROUP, I.

THEORETICAL BACKGROUND (C)

23 JANUARY 1959

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U. S. NAVAL ORDNANCE LABORATORY

WHITE OAK, MARYLAND

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COMPOUNDS CONTAINING THE TERMINAL
FLUORODINITROMETHYL GROUP, I. THEORETICAL BACKGROUND

By

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ABSTRACT: From a number of considerations it is concluded
that a parameter strongly influencing impact sensitivity of
organic high explosives is the entropy of activation in the
decomposition process. Such entropic factors as the steric
conformation about the bond in the molecule which is most
readily broken should therefore play an important role in
determining sensitivity. It is predicted that compounds con-
taining the terminal fluorodinitromethyl group will comprise
a class in which reduced sensitivity to impact may be
achieved without excessive sacrifice in explosive power or
performance.

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This report describes the theoretical background which
serves as a basis for the prediction that compounds containing
the terminal fluorodinitromethyl group will comprise a class
in which reduced sensitivity to impact may be achieved without
excessive sacrifice of explosive power. This work was done
under Task FR-44, "Chemistry of High Energy Compounds".

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COMPOUNDS CONTAINING THE TERMINAL
FLUORODINITROMETHYL GROUP, I. THEORETICAL BACKGROUND

INTRODUCTION

In the history of explosives chemistry continued emphasis
has been placed on the synthesis of explosives of higher and
higher oxygen balance. The theoretical limit in performance of
carbon-hydrogen-nitrogen-oxygen explosives has been approached
with the preparation of numbers of compounds containing more
oxygen per cc than liquid oxygen and with heats of detonation of
1500-1700 cal/g. Without exception these compounds were quite
sensitive and attempts to "desensitize" them with waxes down-
graded their performance almost to the level of current service
explosives*. As a consequence the feeling has grown that extreme
sensitivity to impact is a necessary concomitant of high oxygen
balance. The purpose of the present report is to show that this
is not necessarily the case and to describe a search for families
of pure compounds in which reduced sensitivity might be achieved
without excessive sacrifice of explosive power. This search was
based on a better fundamental understanding of the molecular
processes which take place in decomposition under the impact
hammer.

We have shown (1) that for related families of compounds
there exists a linear relationship between logarithmic 50% impact
heights and a parameter, OB/100, defined as the number of equiva-
lents of oxidant per hundred grams of explosive above the amount
necessary to burn all carbon to carbon monoxide and all hydrogen
to water. An area enclosing the straight line relating these
parameters was defined as the "true trend" for the class of
compounds in question.

That OB/100 is not the only factor influencing impact sensi-
tivity was evidenced by the fact that there were two distinct
and separate "true trends" for the two main classes of polynitro-
aliphatic compounds studied. The one applying to all examples
containing a nitro group bound to nitrogen was described by the
equation, $\log h_{50\%} = 1.38 - 0.18(OB/100) \pm 0.02$. For polynitro-
aliphatics in which the N-nitro group was absent the applicable
expression was, $\log h_{50\%} = 1.76 - 0.22(OB/100) \pm 0.02$.

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* In another report we have shown that "desensitization" by
conventional methods is merely a process of dilution. The same
reduction of sensitivity may be achieved by incorporating the same
number of methylene groups within the structure of the pure chemi-
cal compound as by coating the surfaces of crystals with poly-
methylene waxes (1).

Within one or the other of these categories additional structural features were shown to sensitize or desensitize individual compounds. Thus, for example, 50% impact heights of compounds containing a trinitro or gem-dinitro linkage alpha or beta to another gem-dinitro or sec-nitro group were generally lower than would be predicted from the "true trend" for polynitroaliphatics.

Further evidence that oxidant balance is not the only factor influencing sensitivity was provided by the examples of 1,3-diamino-2,4,6-trinitrobenzene, DATB, and 1,3,5-triamino-2,4,6-trinitrobenzene, TATB. It was predicted (2) that these compounds, which are about equivalent to TNT in both OB/100 and performance, would be less sensitive than TNT because of hydrogen-bending and strong intracrystalline forces. This prediction has been borne out in both cases (3,4).

DISCUSSION

Wenograd (5) has shown striking regularity in an inverse linear relationship between 50% impact heights of explosive molecules and their rates of thermal decomposition extrapolated to 500°, the necessary "hot-spot" temperature according to Bowden (6). It is not a necessary consequence of Wenograd's relationship that the same reactions take place under the impact hammer at 500° as occur in the thermal decomposition at 200°. It is merely required that both processes share the same rate-determining step*.

A strong case can be made that the rate-determining step in a thermal decomposition is the breaking of the first bond in the previously intact molecule. Kinetic theory requires that the first bond broken be the weakest one in that molecule. The factors which determine the rate of this rate-determining step are therefore the energy and entropy of activation in the breaking of the weakest bond, the latter quantity being related directly to the pre-exponential factor A in the Arrhenius equation, $k = A \exp(-\Delta E^*/RT)$.

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* Dacons has shown that the slow thermal decomposition of TNT at 200° yields between 25 and 50 distinct stable compounds. A number of these have been isolated and identified. It seems improbable that all of these are formed as intermediates in the more rapid conversion of TNT to gaseous products under the impact hammer (7).

It is instructive to consider what these quantities mean in the thermal cleavage of an atom to atom linkage. In such a transformation the transition state or activated complex is probably a close approximation of the condition of complete bond rupture. When, of the total molecular energy, a proportion equal to the bond energy of the weakest bond is concentrated within that linkage as vibrational energy, the linkage will break. It follows that the activation energy approximates the energy of the weakest bond plus the kinetic energy of the molecule.

The pre-exponential or entropy factor may be considered as being made up of two terms, $A = PZ$. The Z term, corresponding to the collision number in classical solution kinetics, may be considered as a measure of the number of molecules in the system having as much as or more than the energy represented by ΔE^*. The P term represents the probability that in a given molecule a sufficient proportion of that total energy will be concentrated within the weakest bond as vibrational energy.

To determine the relative contributions of A and E^* to Wenograd's k_{500}°, the following equation applies.

$$\log k_{500}° = \log A - \Delta E^* / 2.303\ RT$$

These quantities are tabulated for a number of explosives in Table I and plotted as functions of $\log h_{50\%}$ in Figure 1 (data from Wenograd) (5). Before considering these data it should be emphasized that they are at best only semi-quantitative. They were derived mainly from measurements of gas evolution as a function of time and there is no assurance that the rate of formation of gas was directly related to the rate of the first or of any single step in what is probably a complex sequence. The reactions were often autocatalytic and the pressure-time decomposition curves were usually of complex sigmoid shape. Arrhenius activation parameters, determined from initial slopes, were consequently subject to large errors. Thus it is not surprising to find different investigators reporting values of $\log A$ differing by as much as 5 and ΔE^* by 5-10 Kcal/mole. It is unfortunate that so little work has been done in the field and that these are the only data available.

TABLE I

ARRHENIUS PARAMETERS FOR THERMAL
DECOMPOSITION AND IMPACT SENSITIVITY

Explosive	log $h_{50\%}$, cm	log A A in sec.$^{-1}$	$\Delta E^\circ/2.303RT$	log k_{500}° k in sec.$^{-1}$
NG	0.90	20.5	13.6	6.9
PETN	1.11	19.8	13.3	6.5
MEDINA	1.11	15.6	10.0	5.6
TNETB	1.26	18.0	12.3	5.7
RDX	1.38	18.5	13.4	5.1
HMX	1.41	19.7	14.9	4.8
TETRYL	1.51	15.4	10.9	4.5
EDNA	1.53	12.8	8.6	4.2
EDDN	1.95	13.1	11.5	1.6
TNT	2.20	12.5	12.3	0.2

It can be seen that log k_{500}° is the comparatively small
difference between two large numbers and that, although the
variation of log $h_{50\%}$ with log k_{500}° is regular, there is no
similar regularity between log $h_{50\%}$ and either of these two large
numbers which combine to make up log k_{500}°. Trends can be ascer-
tained, however, and to facilitate this the areas in Figure 1
enclosing the points for $\Delta E^\circ/RT$ (filled circles) and for log A
(triangles) have been shaded. There appears to be little
direction in the trend for $\Delta E^\circ/RT$ with increasing sensitivity.
Both maximal and minimal values fall at intermediate impact heights.
The trend for log A, on the other hand, appears to show a distinct
direction with maximal values falling at minimal impact heights.
Indeed the "slope" of this trend seems to parallel that of the
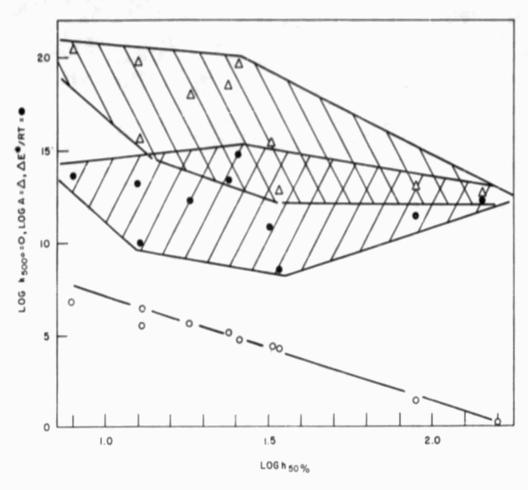log $h_{50\%}$ - log k_{500}° plot.

FIG. I LOG $k_{500°}$ AND THERMODYNAMIC ACTIVATION QUANTITIES
AS FUNCTIONS OF LOG $h_{50\%}$

It may be implied from these observations that a large, if not primary, contributing factor to increasing sensitivity is increasing entropy of activation in the decomposition process. Consideration of the problem from another aspect reinforces this viewpoint. Leffler (8) has shown that on varying a given parameter for a large number of reactions there is a linear relationship of positive slope between entropy of activation and energy of activation. Since the entropy containing term log A is temperature independent and the energy containing term $\Delta E^*/RT$ is temperature dependent, there exists a temperature at which the change in one exactly offsets the change in the other and log k is invariant with the parameter considered. This temperature Leffler defines as the "Isokinetic temperature." Above the Isokinetic temperature the change in rate is in the direction predicted by changing entropy of activation and the reactions are considered as entropy governed; below this temperature the change in rate is in the direction predicted by changing energy of activation, the reactions are considered as energy governed. For the very large majority of organic reactions the Isokinetic temperature falls between 0 and 250°. It would seem highly probable that any reaction which takes place at 500° would be entropy governed.

If there is any validity to these arguments it follows that in determining impact sensitivity an important part is played by such entropic considerations as the steric conformation about the bond being broken in the rate determining step of whatever process takes place under the impact hammer.

The trinitromethyl group may be taken as a specific example. It is bulky and within it there is restriction of rotation about the individual C-nitro linkage, the bond most probably broken in the rate-determining step. The P term in the pre-logarithmic factor of the Arrhenius equation was defined as the probability that sufficient of the total molecular potential energy to cause the rupture of that bond be concentrated within the weakest bond as vibrational energy. When energy is concentrated within a bond it is distributed among vibrations between the bonded atoms and rotation around the bond. The energy going into rotation is not available for bond breaking purposes. Where rotation about the bond is restricted there is a redistribution of energy, less going into rotation more into vibration. The consequence is a greater probability of concentration of vibrational energy, a higher pre-exponential factor, a higher $k_{500}°$ and an increased sensitivity.

The conclusion that internal crowding and restriction of rotation make the trinitromethyl function a sensitizing group leads to the question, "sensitizing with respect to what?" In the NAVORD report on the OB/100 impact sensitivity relationship (1) it was demonstrated that polynitroaliphatics containing this linkage showed higher impact heights at equivalent values of OB/100 than any other class studied, nitramines, nitroaromatics or nitrate esters. In fact, trinitromethyl compounds appear to be less sensitive than any extensive class of organic compounds as yet considered in explosives technology.

The reference category would ideally be one in which at every value of OB/100 there were the same numbers of every type of bond but less restriction of rotation. To achieve reasonable oxidant balances this category would necessarily contain gem-dinitro groups. These would not be in positions alpha or beta to other dinitro or secondary nitro linkages since molecular models show that this structural feature introduces severe internal crowding and, as has been mentioned, greater sensitivity than the trinitromethyl compounds. Several examples of the "ideal" class are available for comparison. Their observed impact heights are listed in Table II together with the impact sensitivities at equivalent values of OB/100 of hypothetical trinitromethyl compounds predicted from the "true trend for polynitroaliphatics" (1). It can be seen that the compounds of the "ideal" class are, indeed, less sensitive.

TABLE II

IMPACT SENSITIVITIES OF
UNCROWDED gem-DINITRO COMPOUNDS

Mol. Formula	Compound	$h_{50\%}$ Actual	$h_{50\%}$ Predicted from "True Trend"
$C_3H_6N_2O_6$	2,2-dinitropropandiol-1,3	110	58
$C_7H_{10}N_4O_{11}$	bis-dinitropropyl carbonate	300	110
$C_8H_{12}N_4O_{10}$	dinitropropyl dinitrovalerate	>320	275
$C_8H_{10}N_4O_{12}$	bis-dinitropropyl oxalate	227	135
$C_3H_6N_2O_5$	2,2-dinitropropanol	>320	80

Unfortunately the requirement that gem-dinitro groups not be alpha or beta to one another limits our ability to devise high oxygen explosives in this "ideal" category. The best we might hope for are compounds balanced to the carbon monoxide level.

An alternative approach involves substituting for one or two of the nitro groups in the trinitromethyl function some other radical which requires less space. The linear cyano group is promising and work along this line is currently under-way (9). Also promising is substitution by the fluorine atom, the subject of the present report.

Several factors in addition to the small size of the fluorine atom contribute to the attractiveness of fluorodinitro compounds. The high heats of formation of hydrogen fluoride and the metal fluorides have already been mentioned (10). From energetic considerations these would be desirable detona-tion products. When attached to the electronegative dinitro-methyl group the fluorine atom is in a comparatively high oxidation state and its bond energy with carbon is undoubtedly lower than the normal C-F bond energy. The fluorine atom in such a molecule may therefore be considered as an equivalent of oxidant which carries its own weight by contributing slightly to the heat of detonation of the self-explosive and substan-tially to the heat of detonation of the metallized explosive.

The question of "carrying its own weight" deserves further amplification. The nitro group is concentrated in oxidant, carrying four equivalents in 46 grams. Replacement by any other group will inevitably lead to decrease in overall oxidant balance of the moelcule. For high oxygen explosives this decrease should be held to a minimum. Shown below are the effects on molecular oxidant balance and on OB/100 of replacing a nitro group by some other function in a hypothetical trinitro-methyl compound of molecular weight 400 and OB/100 = +2.5 (about the CO_2 level).

-Nitro group replaced by-	Δ Mol. Wt.	ΔOB/mole	ΔOB/100
H-	-45	-5	-1.09
CH_3-	-31	-9	-2.23
CN-	-20	-6	-1.45
F-	-27	-3	-0.62

Since they show up quite well in this comparison, fluoro-dinitro compounds were chosen as a class worth studying in the search for desensitizing structural features. The choice was based on the prediction that this class might represent the best readily attainable compromise between energetic and entropic considerations. The synthesis of thirteen members of this new family of compounds and the test of this prediction that improved sensitivity could be achieved without excessive sacrifice of oxidant balance are described in the accompanying NAVORD Report No. 6207. (10)

ACKNOWLEDGMENTS

BIBLIOGRAPHY

(1) M. J. Kamlet, NAVORD Report 6126, "A Correlation of Impact Sensitivities of Explosives with Oxidant Balances", 26 September 1958. CONFIDENTIAL *AD- 304 071*

(2) NOLR 1228, "Foundational Research Progress Report, 1957", p. 46. *AD-162061*

(3) K. G. Shipp and M. E. Hill, NAVORD Report 6016, "Heat Resistant Explosives, II. 1,3-Diamino-2,4,6-trinitrobenzene, DATB", 31 March 1958. CONFIDENTIAL *AD-162 976*

(4) L. A. Kaplan and F. T. Taylor, Jr., NAVORD Report 6017, "High Temperature Stable Explosives, I. Process Development Study of 1,3,5-Triamino-2,4,6-trinitrobenzene", 10 March 1958. CONFIDENTIAL *AD-162 977*

(5) J. Wenograd, NAVORD Report 5730, "Sensitivity of Explosives, IV. The Correlation of the Impact Sensitivities of High Explosives with Their Thermal Decomposition Rates", 30 September 1957. CONFIDENTIAL *AD-116 047*

(6) F. P. Bowden and A. D. Yoffee, "Initiation and Growth of Explosions in Liquids and Solids", Cambridge University Press, 1952.

(7) Private Communication, Dr. J. C. Dacons, Naval Ordnance Laboratory.

(8) J. D. Leffler, J. Org. Chem., 20, 1202 (1955).

(9), Private Communication, Dr. T. Hall, Naval Ordnance Laboratory.

(10) M. J. Kamlet, NAVORD Report 6207, "Compounds Containing the Terminal Fluorodinitromethyl Group, II. A New Class of Organic High Explosives." CONFIDENTIAL *AD. 307 472*